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Chapter 1

Fragrances, Flavors, and Food Additives

THE PERFUME¹ INDUSTRY

The manufacture of perfume, cologne, and toilet water, collectively known as the fragrances has undergone drastic changes in the past quarter century, prior to which perfumers were usually trained through apprenticeships in laboratories until, working with traditional materials in well-defined patterns, they achieved skill in mixing and blending. Only occasionally was a new and original odor developed, such as Old Spice, which immediately won spontaneous and favorable response from consumers. Not many people realize how complex the creation of an acceptable fragrance has become; it requires professional knowledge, skill, and experience, coupled with specialization in synthetic chemistry's technical problems, followed by consumer panel testing. This change has resulted from a number of factors, for example: (1) increase in the number of available raw-material ingredients, both natural and synthetic; (2) a variety of new types of products requiring fragrances; (3) innovations in packaging, especially aerosol sprays, virtually nonexistent before 1950, and other new forms of dispensing such as perfume powders, cream sachets, gels, lotions, and sticks; (4) broadened channels and methods of distribution, including door-to-door selling; and (5) phenomenal growth in men's toiletries. These numerous recent developments are in contrast to the two main changes which took place earlier, the introduction of synthetics and improved methods of obtaining true oils.

Perfume takes its name from the Latin word *perfumare* (to fill with smoke), since in its original form it was incense burned in Egyptian temples. Early incenses were merely mixtures of finely ground spices held together by myrrh or storax. The next advance was the discovery that, if certain spices and flowers were steeped in fat or oil, the fat or oil would retain a portion of the odoriferous principle. Thus were manufactured the ointments and fragrant unguents of Biblical fame. Avicenna, the Arabian physician, discovered steam distillation of volatile oils. During his search for medical potions, he found that flowers boiled in an alembic with water gave up some of their essence to the distillate. The returning Crusaders brought to Europe all the art and skill of the orient in perfumery, as well as information relating to sources of gums, oils, and spices. René, perfumer to Catherine de' Medici, invented many new confections to delight the queenly nose and, in his spare time, was one of the cleverest and deadliest of the famous de' Medici poisoners. Many of the finest perfumes are imported from France. Classical colognes are at least 200 years old, having originated in

¹ECT, 3d ed., vol. 16, 1982, p. 947.

Cologne, Germany; they were probably the first imports into this country. It was not until the 1950s that U.S. industry discovered that the sale of perfume odors in an alcohol-diluted form was profitable.

USES AND ECONOMICS. Fragrance shipments were \$1800 million in 1981, and this was a large increase from the \$320 million in 1974. The popularity of men's fragrances has, no doubt, contributed greatly to the increase.

Fragrances make a major contribution to the cosmetic industry, second only to the amount used in soaps and detergents. Fragrances are used industrially in masking, neutralizing, and altering the odor of various products, as well as in creating a distinctive aroma for normally odorless objects. Cashmere shawls manufactured in Scotland are given the Hindu touch by a trace of patchouli oil applied to them. Aromatics, sometimes referred to as *reodorants*, are added to fabric sizing to disguise the glue or casein smell, leaving the product with a fine fresh odor. Leather goods and papers are scented delicately to eliminate the raw-material smell. The odor of kerosene in fly sprays is masked; artificial cedarwood is made by coating other woods with cedar oil reclaimed in pencil manufacturing. Canneries, rendering plants, municipal refuse plants, and food processing systems are other areas where reodorants are used. Paint odor during drying is masked by essential oils and fixatives introduced in small quantities in the bulk product. Odors are used successfully to increase customer appeal, though they are not essential to the performance of the products to which they are added.² A minute amount of bornyl acetate evaporated in an air-conditioning system imparts an outdoor tang to the air.

Constituents

A perfume may be defined as any mixture of pleasantly odorous substances incorporated in a suitable vehicle. Formerly, practically all the products used in perfumery were of natural origin. Even when humans first started synthesizing materials for use in this field, they endeavored to duplicate the finest in nature. There has been a marked tendency in recent years, however, to market perfumes which have no exact counterpart in the floral kingdom but which have received wide acceptance. The finest modern perfumes are neither wholly synthetic nor completely natural. The best product of the art is a judicious blend of the two in order to enhance the natural perfume, to reduce the price, and to introduce fragrances into the enchanting gamut at present available. A product made solely of synthetics tends to be coarse and unnatural because of the absence of impurities in minute amounts which finish and round out the bouquet of natural odors; however, such an eventual development is predicted. The chemist has also succeeded in creating essences of flowers which yield no natural essence or whose essence is too expensive or too fugitive to make its extraction profitable. Lily of the valley, lilac, and violet are examples. The constituents of perfumes are: the vehicle or solvent, the fixative, and the odoriferous elements.

VEHICLES. The modern solvent for blending and holding perfume materials is highly refined ethyl alcohol mixed with more or less water according to the solubilities of the oils employed. This solvent, with its volatile nature, helps to project the scent it carries, is fairly inert to the

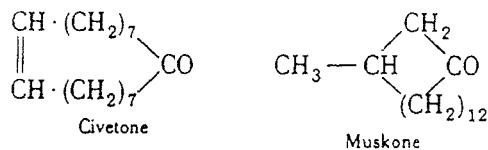
²Mitchell et al., "Importance of Odor as a Nonfunctional Component," Odor Symposium, New York Academy of Sciences, November 7-9, 1963.

solutes, and is not too irritating to the human skin. The slight natural odor of the alcohol is removed by deodorizing, or "prefixation," of the alcohol. This is accomplished by adding a small amount of gum benzoin or other resinous fixatives to the alcohol and allowing it to mature for a week or two. The result is an almost odorless alcohol, the natural rawness having been neutralized by the resins.

FIXATIVES. In an ordinary solution of perfume substances in alcohol, the more volatile materials evaporate first, and the odor of the perfume consists of a series of impressions rather than the desired ensemble. To obviate this difficulty, a fixative is added. Fixatives may be defined as substances of lower volatility than the perfume oils, which retard and even up the rate of evaporation of the various odorous constituents. The types of fixative considered are animal secretions, resinous products, essential oils, and synthetic chemicals. Any of these fixatives may or may not contribute to the odor of the finished product but, if they do, they must blend with and complement the main fragrance.

Animal Fixatives. Of all animal products, *castor*, or *castoreum*, a brownish orange exudate of the perineal glands of the beaver, is employed in the greatest quantity. Among the odoriferous components of the volatile oil of castor are benzyl alcohol, acetophenone, *l*-bornone, and castorin (a volatile resinous component of unknown structure).

Civet is the soft, fatty secretion of the perineal glands of civet cats, which are indigenous to many countries, and was developed in Ethiopia. The secretions are collected about every 4 days by spooning and are packed for export in hollow horns. The crude civet is disagreeable in odor because of the skatole present. On dilution and aging, however, the skatole odor disappears, and the sweet and somewhat floral odor of civetone, a cyclic ketone, appears.



Musk is the dried secretion of the preputial glands of the male musk deer, found in the Himalayas. The odor is due to a cyclic ketone called *muskone*, which is present to the extent of from $\frac{1}{2}$ to 2%. Musk, the most useful of the animal fixatives, imparts body and smoothness to a perfume composition even when diluted so that its own odor is completely effaced. Musk is used for its own sake in heavy oriental perfumes.

Ambergris is the least used, but probably best known, of the animal fixatives. It is a calculus, or secretion, developed by certain whales. Ambergris is obtained by cutting open the captured whale, or it is obtained from whales stranded on a beach. It is waxy in consistency, softening at about 60°C, and may be white, yellow, brown, black, or variegated like marble. It is composed of 80 to 85% ambrein (triterpenic tricyclic alcohol), resembling cholesterol and acting merely as a binder, and 12 to 15% ambergris oil, which is the active ingredient. It is employed as a tincture, which must be matured before it is used. The odor of the tincture is decidedly musty and has great fixative powers.

Musc zibata is the newest animal fixative, derived from glands of the Louisiana muskrat. It was only during World War II that musc zibata was commercialized. About 90% of the unsaponifiable material in muskrat glands consists of large, odorless cyclic alcohols, which are converted to ketones, increasing the characteristic musk odor nearly 50 times. It is a replacement for, or an addition to, Asiatic musk.

Resinous Fixatives. Resinous fixatives are normal or pathological exudates from certain plants, which are more important historically than commercially. These are hard resins, e.g., benzoin and gums; softer resins, e.g., myrrh and labdanum; balsams, moderately soft, e.g., Peru balsam, tolu balsam, copiaba, and storax; oleoresins, oily materials, e.g., terpenes: extracts from resins, less viscous, e.g., ambrein. All these substances, when being prepared for perfume compounding, are dissolved and aged by methods passed down by word of mouth. If solution is brought about in the cold, the mixture is called a *tincture*. If heat is required to give solution, the mixture is an *infusion*. Alcohol is the solvent, sometimes aided by benzyl benzoate or diethyl phthalate. The most important of the soft gums is *labdanum*. The leaves of a plant growing in the Mediterranean area exude this sticky substance. An extract from this gum has an odor suggestive of ambergris and is marked as *ambrein*, having extremely good fixative value. Of the harder plant resins used in perfumes, *benzoin* is the most important. The history of chemistry was influenced by this substance. The early source of benzoin was Java, where it was called *luban jawi*. Through various contractions and linguistic modifications, it became "banjawi," "benjui," "benzoi," "benzoin," and "benjamin." In early organic chemical history an acid isolated from this gum became known as *benzoic acid*, from which compound the names of all benzo compounds of today are derived.

Essential-Oil Fixatives. A few essential oils are used for their fixative properties as well as their odor. The more important of these are clary sage, vetiver, patchouli, orris, and sandalwood. These oils have boiling points higher than normal (285 to 290°C).

Synthetic Fixatives. Certain high-boiling, comparatively odorless esters are used as fixatives to replace some imported animal fixatives. Among them are glycetyl diacetate (259°C), ethyl phthalate (295°C), and benzyl benzoate (323°C). Other synthetics are used as fixatives, although they have a definite odor of their own that contributes to the ensemble in which they are used. A few of these are

Amyl benzoate	Musk ketone	Heliotropin
Phenethyl phenylacetate	Musk ambrette	Hydroxycitronellal
Cinnamic alcohol esters	Benzophenone	Indole
Cinnamic acid esters	Vanillin	Skatole
Acetophenone	Coumarin	

ODOROUS SUBSTANCES. Most odorous substances used in perfumery come under three headings: (1) essential oils, (2) isolates, and (3) synthetic or semisynthetic chemicals.

Essential Oils.³ Essential oils may be defined as volatile, odoriferous oils of vegetable origin (Table 1.1). A distinction should be made, however, between natural flower oils obtained by enfleurage or solvent extraction and essential oils recovered by distillation. Distilled oils may lack some component which is not volatile enough or which is lost during distillation. Two notable examples of this are rose oil, in which phenylethyl alcohol is lost to the watery portion of the distillate, and orange flower oil, in which the distilled oil contains

³"Essential" does not mean "most necessary" but rather the concentrated characteristic or quintessence of a natural flavor or fragrance raw material; *International Standardization of Essential Oils*, Committee ISO/TC54 publishes standards. See *Cosmet. Perfum.* 90 (2) 86 (1975).

Table 1.1 Important Essential Oils

Name of Oil	Important Geographical Sources	Method of Production	Part of Plant Used	Chief Constituents
Almond, bitter	California, Morocco	Steam	Kernels	Benzaldehyde 96-98%, HCN 2-4%
Bay Bergamot	West Indies Southern Italy	Steam Expression	Leaves Peel	Eugenol 50% Linalyl acetate 40%, linalool 6%
Caraway	Northern Europe, Holland	Steam	Seed	Carvone 55%, <i>d</i> -limonene
Cassia (Chinese cinnamon)	China	Steam	Leaves and twigs	Cinnamic aldehyde 70%
Cedarwood	North America	Steam	Red core wood	Cedrene, cedar
Cinnamon	Ceylon	Steam	Bark	Cinnamic aldehyde, eugenol
Citronella, Java	Java, Ceylon	Steam	Grass	Geraniol 65%, citronellal
Clove	Zanzibar, Madagascar, Indonesia	Steam	Buds (cloves)	Eugenol 85-95%
Coriander	Central Europe, Russia	Steam	Fruit	Linalool, pinene
Eucalyptus	California, Australia	Steam	Leaves	Cineole (eucalyptole) 70-80%
Geranium	Mediterranean countries	Steam	Leaves	Geraniol esters 30%, citronellol
Jasmine	France, Egypt, Italy	Cold pomade	Flowers	Benzyl acetate, linalool, and esters
Lavender	Mediterranean area	Distillation	Flowers	Linalool
Lemon	California, Sicily	Expression	Peel	<i>d</i> -Limonene 90%, citral 3.5-5%
Orange, sweet	Florida, California, Mediterranean area	Expression, distillation	Peel	<i>d</i> -Limonene 90%
Peppermint	Michigan, Indiana, etc.	Steam	Leaves and tops	Menthol 45-90% and esters
Rose	Bulgaria, Turkey	Steam, solvent, enfleurage	Flowers	Geraniol and citronellol 75%
Sandalwood	India, East Indies	Steam	Wood	Santalol 90%, esters 3%
Spearmint	Michigan, Indiana	Steam	Leaves	Carvone 50-60%
Tuberose	France	Enfleurage, solvent extraction	Flowers	Tuberose oil
Wintergreen (gaultheria)	Eastern United States	Steam	Leaves	Methyl salicylate 99%
Ylang-ylang	Madagascar, Philippines	Steam, solvent extraction	Flowers	Esters, alcohols

but a very small proportion of methyl anthranilate, whereas the extracted flower oil may contain as much as one-sixth of this constituent.

Essential oils are, in the main, insoluble in water and soluble in organic solvents, although enough of the oil may dissolve in water to give an intense odor to the solution, as in the case of rose water and orange flower water. These oils are volatile enough to distill unchanged in most instances, and are also volatile with steam. They vary from colorless to yellow or brown in color. An essential oil is usually a mixture of compounds, although oil of wintergreen is almost pure methyl salicylate. The refractive indexes of the oils are high, averaging about 1.5. The oils show a wide range of optical activity, rotating in both directions.

The compounds occurring in essential oils may be classified as follows:

1. **Esters.** Mainly of benzoic, acetic, salicylic, and cinnamic acids.
2. **Alcohols.** Linalool, geraniol, citronellol, terpinol, menthol, borneol.
3. **Aldehydes.** Citral, citronellol, benzaldehyde, cinnamaldehyde, cuminic aldehyde, vanillin.
4. **Acids.** Benzoic, cinnamic, myristic, isovaleric in the free state.
5. **Phenols.** Eugenol, thymol, carvacrol.
6. **Ketones.** Carvone, menthone, pulegone, irone, fenchone, thujone, camphor, mentyl nonyl ketone, methyl heptenone.
7. **Esters.** Cineole, internal ether (eucalyptole), anethole, safrole.
8. **Lactones.** Coumarin.
9. **Terpenes.** Camphene, pinene, limonene, phellandrene, cedrene.
10. **Hydrocarbons.** Cymene, styrene (phenylethylene).

In living plants essential oils are probably connected with metabolism, fertilization, or protection from enemies. Any or all parts of the plant may contain oil. Essential oils are found in buds, flowers, leaves, bark, stems, fruits, seeds, wood, roots, and rhizomes and in some trees in oleoresinous exudates.

Volatile oils may be recovered from plants by a variety of methods: 1. expression, 2. distillation, 3. extraction with volatile solvents, 4. enfleurage, and 5. maceration. The majority of oils are obtained by distillation, usually with steam, but certain oils are adversely affected by the temperature. Distilled citrus oils are of inferior quality, therefore they are derived by expression. For certain flowers which yield no oil upon distillation or else deteriorated oil, the last three methods are used. However, extraction with volatile solvents, a comparatively recent process, has superseded maceration (extraction with hot fat) for all practical purposes and is replacing enfleurage. Solvent extraction is the most technically advanced process and yields truly representative odors, but is more expensive than distillation.

Distillation, usually with steam. Flowers and grasses are normally charged into the still without preparation. Leaves and succulent roots and twigs are cut into small pieces. Dried materials are powdered. Woods and tough roots are sawed into small pieces or mechanically chipped. Seeds and nuts are fed through crushing rolls spaced so as to crack them. Berries are charged in the natural state, since the heat of distillation soon develops enough pressure to burst their integument. The stills employed in factories are of copper, tin-lined copper or stainless steel and of about 2300 L capacity. They are provided with condensers of various sorts, tubular ones being the more efficient, and with a separator for dividing the oily layer from the aqueous one. Although removable baskets for holding the material to be distilled are used, the better procedure seems to be to construct the still with a perforated false plate lying just above the bottom. Underneath this false bottom are steam coils, both closed and

⁴Dorland and Rogers, *The Fragrance and Flavor Industry*, Dorland, Mendham, N.J., 1977.

perforated. In operating these stills, the charge is heated by steam in both the closed and the open pipes, thus effecting economical steam distillation. The aqueous layer in the condensate frequently carries, in solution, valuable constituents, as in the case of rose and orange flower oil, and is consequently pumped back into the still to supply some of the necessary water. Steam distillation usually is carried out at atmospheric pressure. If the constituents of the oil are subject to hydrolysis, the process is carried out in a vacuum. Much distillation for essential oils is done at the harvest site in extremely crude stills. These stills are converted oil drums or copper pots equipped with pipe condensers running through water tubs. The material and water are charged into the still, and a direct fire of dried material exhausted in previous distillations is built underneath. The efficiency is low, and the oil is contaminated with pyrolysis products, such as acrolein, trimethylamine, and creosotelike substances. The crude oils obtained from the stills are sometimes further treated before use by vacuum-rectification, by fractional freezing (e.g., menthol from Japanese peppermint oil), by washing with potassium hydroxide to remove free acids and phenolic compounds, by removal of wanted or unwanted aldehydes and ketones through formation of the bisulfite addition compounds, or by formation of specific insoluble products, as in the reaction of calcium chloride with geraniol.

Expression by machine can yield an oil almost identical to the hand-pressed product, and is the method used commercially. Of the hand-pressed processes, the *sponge* process is the most important, since it produces the highest-quality oil. Here the fruit is halved, and the peel trimmed and soaked in water for several hours. Each peel is pressed against a sponge, and the oil is ejected into the sponge, which is periodically squeezed dry. One person can prepare only 680 g of lemon oil a day by this method, but it is still practiced, especially in Sicily.

Enfleurage. The enfleurage process is a cold-fat extraction process used on a few types of delicate flowers (jasmine, tuberose, violet, etc.) which yield no direct oil at all on distillation. In the case of jasmine and tuberose, the picked flowers continue to produce perfume as long as they are alive (about 24 h). The fat, or base, consists of a highly purified mixture of 1 part tallow to 2 parts lard, with 0.6% benzoin added as a preservative. This method is no longer used commercially.

Extraction with volatile solvents. The most important factor in the success of this practice is the selection of the solvent. The solvent must (1) be selective, i.e., quickly and completely dissolve the odoriferous components, but have only a minimum of inert matter, (2) have a low boiling point, (3) be chemically inert to the oil, (4) evaporate completely without leaving any odorous residue, and (5) be low-priced and, if possible, nonflammable. Many solvents have been used, but highly purified petroleum ether is the most successful, with benzene ranking next. The former is specially prepared by repeated rectification and has a boiling point no higher than 75°C. When benzene is employed, it is specially purified by repeated crystallization. The *extraction equipment* is complicated and relatively expensive and consists of stills for fractionating the solvent, batteries for extracting the flowers, and stills for concentrating the flower-oil solutions. The two types of extractors employed are the stationary and rotary types.

In the rotary process the oil is extracted on the *countercurrent principle*. The 1325-L steam-jacketed drums revolve around a horizontal axis and are divided into compartments by perforated plates at right angles to the axis. About 135 kg of flowers is charged into the first drum, along with 575 L of petroleum ether which has already come through the other two drums. The drum and its contents are rotated for an hour cold and for an additional half hour with steam in the jacket. The saturated solvent is pumped to the recovery still, and the flowers in the drum are treated twice more, the second time with once-used solvent and the last time with fresh solvent from the recovery still. The exhausted flowers are blown with

steam to recover the adhering solvent. About 90 percent of the solvent is boiled off at atmospheric pressure, and the rest is removed under vacuum. After the solvent is removed in either process, the semisolid residue contains the essential oil, along with a quantity of waxes, resins, and coloring material from the blossoms. This pasty mass is known as *concrete*. In turn it is treated with cold alcohol in which most of the wax and resin are insoluble. The small amount of unwanted material that dissolves is removed by cooling the solution to -20°C and filtering it. The resulting liquid contains the essential oil and some of the ether-soluble color of the flower and is known as an *extract*. When the alcohol has been removed, an *absolute* remains.

In some oils there is a large quantity of *terpenes*. This is especially true in the case of lemon and orange oils, which have as much as 90% *d*-limonene in their normal composition. Not only are terpenes and sesquiterpenes of exceedingly little value to the strength and character of the oils, but they also oxidize and polymerize rapidly on standing to form compounds of a strong turpentine-like flavor. Furthermore, terpenes are insoluble in the lower strengths of alcohol used as a solvent and make cloudy solutions which are cleared up only with difficulty. Hence it is desirable to remove terpenes and sesquiterpenes from many oils. Such an oil, orange, for example, is 40 times as strong as the original and makes a clear solution in dilute alcohol. The oil has now very little tendency to rancidify, although it has not quite the freshness of the original. These treated oils are labeled "tsf" (terpene- and sesquiterpene-free). Because each oil has a different composition, *deterpenation* requires a special process. Two methods are involved, either the removal of the terpenes, sesquiterpenes, and paraffins by fractional distillation under vacuum, or extraction of the more soluble oxygenated compounds (principal odor carriers) with dilute alcohol or other solvents.

Because of the complex nature and the high price commanded by so many essential oils, a great deal of adulteration, or sophistication, is practiced. These additions were formerly extremely hard to detect in most cases since, whenever possible, a mixture of adulterants is used that does not change the physical constants of the oil. Common agents used are alcohol, cedar oil, turpentine, terpenes, sesquiterpenes, and low specific gravity liquid petroleums. The advent of so many esters of glycol and glycerol on the market increased the difficulty of detection, since these compounds are colorless and practically odorless and in the right combination can be made to simulate almost any specific gravity and refractive index specifications set up for the oil they are intended to adulterate. The modern use of gas chromatography (GC) has made it possible to detect easily even small amounts of adulterants. Rose oil may be sophisticated with geraniol or a mixture of geraniol and citronellol; wintergreen and sweet birch oil are mixed with large amounts of synthetic methyl salicylate; and lemon oil is often "stretched" considerably with citral from lemon grass oil.

Isolates. Isolates are pure chemical compounds whose source is an essential oil or other natural perfume material. Notable examples are eugenol from clove oil, pinene from turpentine, anethole from anise oil, and linalool from linaloa oil (bois de rose).

SYNTHETICS AND SEMISYNTHETICS USED IN PERFUMES AND FLAVORS.⁵ More and more important constituents of perfumes and flavors are being made by the usual chemical synthetic procedures. Compositions containing predominantly inexpensive synthetics now account for more than 50 percent of the fragrances used in perfumes. Some constituents are chemically synthesized from an isolate or other natural starting materials and are classed as

⁵ Poucher, *Perfumes, Cosmetics and Soaps*, vol. II, Wiley, New York, 1974; Clark and Grande, Study of Odor Variation with Structural Change, *Cosmet. Perfum.* 90 (6) 58 (1975); Chemicals from Trees, *CHEMTECH*, 5 236 (1975).